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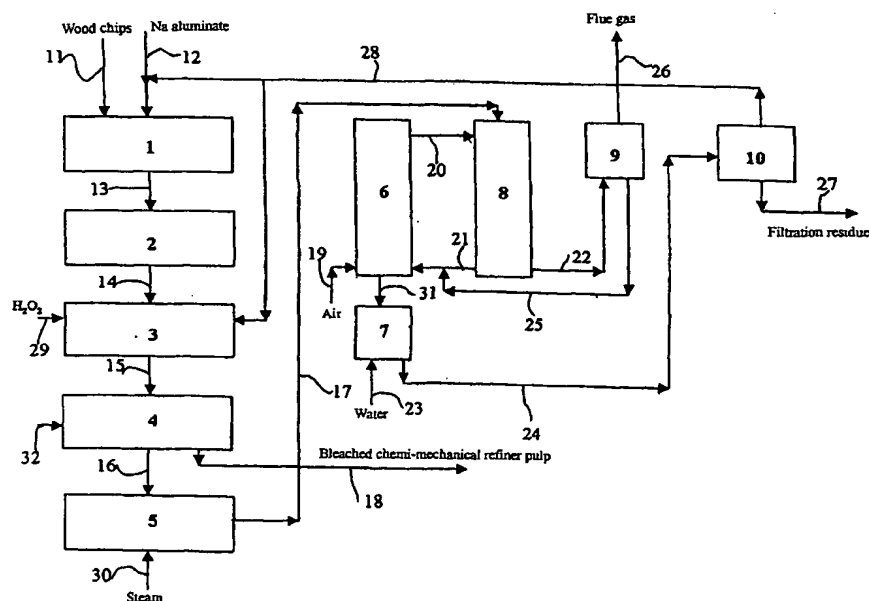
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(54) Title: METHOD FOR BLEACHING MECHANICALLY DEFIBERED PULP



(57) Abstract: The invention relates to a method for bleaching (3) mechanically defibered pulp (14) with peroxide in alkaline conditions and for washing (4) the bleached pulp (15) and recovering chemicals from the spent liquor (16) of the bleaching step by concentrating (5,8) and combusting (6) the spent liquor and subsequently dissolving (7) the ash thus formed into water (13). According to the invention, the alkaline conditions of the bleaching step are obtained by adding sodium aluminate (12) to the pulp (14) to be bleached, at least a part of the added sodium aluminate being said ash (28) dissolved in water.

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## Method for bleaching mechanically defibered pulp

5 The present invention relates to a method for bleaching mechanically defibered pulp and particularly to a method for bleaching mechanically defibered pulp with peroxide in an alkaline, that is, a basic environment and for washing the bleached pulp, as well as for recovery of chemicals from the spent liquor of the bleaching process by concentrating the liquor, combusting the concentrated liquor and dissolving the ash resulting from the combustion into water.

10

Wood can be processed chemically or mechanically to receive fibers suitable for papermaking. In chemical processes, lignin that binds the fibers of wood together is dissolved in a chemical process at an elevated temperature and pressure. The chemical solution may be either acid or basic. Nowadays, generally an alkaline cooking process known as sulfate cooking is used having NaOH and Na<sub>2</sub>S as cooking chemicals. Pulp yield prior to bleaching is about 50 %. Soluble wood substance and cooking chemicals are recovered from the fiber washing step as a solution having a total solids content above 10 % the remainder being water. This spent liquor is concentrated by evaporation, whereupon it is combusted in a chemical recovery boiler. The heat content of organic matter dissolved from wood is recovered as high-pressure steam, from which electricity and process steam of a lower pressure is produced, generally by means of a turbogenerator. The chemicals form a melt at the bottom of the recovery boiler, which melt is dissolved in water and then converted by a conventional causticizing process into cooking chemicals suitable for reuse.

25

A cost-effective production of sulfate pulp necessitates the above-described combustion of spent liquor and recovery of chemicals by causticizing, requiring equipments involving very high investment costs.

30

In mechanical defibering processes the yield is 90 % to 97 % calculated on wood. Thermo mechanical pulping process, i.e. the TMP process, is generally integrated with the paper mill facilities. The chemical oxygen demand (COD) of this process is

50 to 80 kg/ton pulp produced. The wastewater of the process is taken to a biological treatment process in conjunction with other wastewaters of the paper mill.

5 Chemi-mechanical refining or CTMP plants are not equally often integrated with a paper mill, but rather, the produced pulp is bleached, dried and transported for use elsewhere. The chemical oxygen demand of wastewater from this process may be even twice as compared to conventional mechanically defibred pulp, whereby also the waste water treatment cost in a biological treatment plant is roughly doubled. Furthermore, spent chemicals cannot be recovered, but instead, they are often  
10 dumped in nearby waterways thus forming an environmental hazard.

The CTMP process produces fibers at a high yield, which fibers in some applications can replace sulfate pulp. Moreover, the fiber yield is clearly higher and the investment costs in relation to production capacity is substantially lower than in a sulfate  
15 pulping process.

In a CTMP plant, chips are impregnated with a  $\text{Na}_2\text{SO}_3$  solution. Generally, chemical consumption is about 20 kg/ton pulp. After grinding, the pulp is bleached using about 20 kg  $\text{H}_2\text{O}_2$ /ton pulp together with an equal amount of NaOH.  
20

If a chemical recovery process of the type used in sulfate pulp plants would be available to plants producing bleached chemi-mechanical refiner pulp, the overall competitive edge of a CTMP plant could be improved and the environmental load of the plant could be reduced.  
25

The first steps in this direction at a full-scale plant level have already been taken in a Canadian plant producing bleached chemi-mechanical refiner pulp from aspen. The produced pulp is dried and sold.

30 In this plant, impregnation is carried out with a sodium sulfite solution and bleaching is carried out with alkaline peroxide. The spent liquors from both steps are concentrated by evaporation and the thus received concentrated liquor is combusted in a

recovery boiler, wherein the dissolved organic matter is burned to carbon dioxide, while the spent sodium and sulfur chemicals are reduced to a melt of  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{CO}_3$ . In this known process, the melt is cooled and stored for possible later use. Since both compounds are water-soluble, they must be stored in dry conditions.

5

Industrial use of a pulping process known as the Sonoco process is described in publication Appita, Vol. 33, no. 6, pp. 447-453. The fiber to be produced herein is a so-called NSSC pulp produced by impregnating a  $\text{Na}_2\text{SO}_3$  solution at elevated pressure and temperature into the chips in a continuous digester. After cooking, the defibering is carried out in a refiner. Pulp yield is about 80 % of the wood. The active chemical used in the process is the same as in a CTMP process. According to the publication, chemical recovery is implemented by adding aluminum hydroxide to the evaporation process prior to final concentration. Additionally, recycled sodium aluminate is added to the strong spent liquor and this mixture is pelletized. The pellets are combusted in a rotary recuperative furnace having a discharge-end temperature of above 900 °C. Reducing conditions prevail in the interior of the pellets and the sulfur of the spent liquor is reduced to sulfide, and simultaneously sodium and aluminum form a stable sodium aluminate having a high melting temperature (1600 °C). Sulfur is released from the pellet as  $\text{H}_2\text{S}$  and is immediately oxidized to  $\text{SO}_2$ . A part of the combusted pellets are crushed and recirculated to the pelletization of strong spent liquor. The remaining part of the aluminate pellets is dissolved. Sodium aluminate is water-soluble and forms a strong alkaline liquor. The  $\text{SO}_2$  of the flue gases is absorbed into this liquor, whereby  $\text{Na}_2\text{SO}_3$  is formed and the aluminum hydroxide precipitates.

25

The  $\text{Na}_2\text{SO}_3$  is reused for impregnation and the aluminum hydroxide is added to the evaporation phase of spent liquor.

30

Generally, the literature of the art teaches that production of a CTMP pulp requires sulfonation of lignin in the impregnation phase, that is, use of sulfite, and the pulp is normally bleached using peroxide, which process needs alkaline conditions. Conventionally,  $\text{NaOH}$  is used for controlling the pH. The recovery of the heat content of the

organic matter dissolved from wood requires such a high temperature that the chemicals used in the process melt at that temperature. Efficient recovery of heat and chemicals from such a melt is very demanding and requires expensive equipment investments. Consequently it would be particularly desirable to find a bleaching process, and preferably also an associated defibering method, wherein such chemicals could be used which will not melt during combustion of concentrated spent liquors received from the bleaching and, preferably, also from the defibering process, when heat and chemicals are to be recovered from said liquors.

It is an object of the present invention to provide such a method, the main features of the present invention being disclosed in the accompanying claims and especially in claim 1. The other claims disclose preferred embodiments of the invention as examples of different ways to apply the invention. However, the invention is not limited to these exemplary embodiments.

Sodium aluminate is extremely alkaline, so it can be used instead of NaOH in peroxide bleaching of defibered pulp. Further, the melting point of sodium aluminate is so high that it will not melt in combusting concentrated spent liquors for recovering heat and chemicals, but instead it forms ash, which is readily dissolvable in water, in order to be recirculated.

Because the alkaline bleaching conditions according to the invention is provided by adding strongly alkaline sodium aluminate instead of NaOH into the pulp to be bleached with peroxide, it is particularly advantageous to impregnate chips to be mechanically defibered with an aqueous solution of sodium aluminate, which subsequently to the mechanical refining step is passed to the bleaching step together with the pulp to be bleached. Sodium aluminate impregnated and defibered pulp is clearly stronger than that of sulfonated and defibered pulp. In the impregnation of chips to be mechanically defibered sodium aluminate is used, which at least partially is obtained by combusting concentrated spent liquor and by dissolving the received ash.

In a preferred embodiment of the invention, bleaching is carried out at a temperature of about 20-150 °C, advantageously 50-100 °C, and at a pH of about 9.5-12.5, advantageously 10-12.

5 The concentrated spent liquors from the bleaching, and advantageously from the defibering, can be combusted at a very high temperature of about 500-1100 °C without the risk that the chemicals used in the bleaching or in the impregnation would form a melt. Prior to the combustion, the sodium aluminate containing spent liquors obtained from the bleaching step and possibly from the defibering step are  
10 advantageously concentrated to a solids content of at least about 30 %, and preferably up to 35-45 %. Further concentration of concentrated waste liquor is advantageously performed by using hot flue gases received from the combustion of concentrated spent liquor, e.g., in a spray evaporator.

15 If the spent liquor contains sulfur compounds, they can be bound to  $\text{CaSO}_4$  during the combustion in a known way by adding a suitable lime product, such as ground limestone, to the spent liquor to be combusted.

To a person skilled in the art it is obvious that the method according to the invention  
20 can be utilized with sodium aluminate or in lieu thereof also any other alkali metal aluminate. However, sodium aluminate is a chemical of an attractive price and easy availability that is generally used, among other applications, in the purification of raw water and wastewaters. It is further obvious that also with an alkali metal aluminate or in lieu thereof can be used any other sufficiently alkaline chemical having a  
25 sufficiently high melting temperature, such as titanates or ferrites.

The mechanical defibering preceding the bleaching step according to the invention can be carried out as a using thermo-mechanical or chemi-mechanical refiner process in one or several steps in a way known as such. If the chips are impregnated with an  
30 aqueous solution of sodium aluminate prior to defibering, the ground pulp can be passed directly to the peroxide bleaching step without intermediate washing of the pulp and separation of wash waters.

It is a major benefit of the method according to the invention that it is compatible with all fibrous plant raw materials and, particularly, all wood species.

5 In the following, the invention is disclosed closer by means of examples and by referring to the appended drawing showing the block diagram of a process suiting particularly well to carry out the method according to the invention, which process, however, represents only one of many possible embodiments of the invention.

10 Wood chips 11 and an aqueous solution of Na aluminate are fed to an impregnation step 1, wherefrom the impregnated chips are led through a pipe 13 to a mechanical defibering or grinding step 2 carried out by means of one or several disc refiners, connected in series.

15 Subsequently the defibered pulp together with the impregnating chemicals is passed through in a pipe 14 to a bleaching step 3, to which also peroxide 29 and more aqueous solution of Na aluminate 28 are added. Bleaching is carried out at an elevated temperature and by feeding such an amount of Na aluminate 28 to the bleaching step 3 that strongly alkaline bleaching conditions are obtained. Subsequently, the  
20 bleached pulp is passed through a pipe 15 to a washing step 4, to which also wash water 32 is fed and from which step the bleached chemi-mechanical refiner pulp 18 is discharged and the spent liquor 16 is passed to an evaporation step 5, wherein the liquor is first concentrated by means of steam 30 and then it is further concentrated 8 with hot flue gases 20 when the concentrated spent liquor has been passed through a  
25 pipe 17 to a spray-evaporation step 8, to which also hot flue gases are passed from a circulating-bed furnace 6. The moist flue gases leaving the spray-evaporation step through a pipe 22 is further filtered in a dust filter 9 before they are discharged 26 from the process, while the dust collected in the dust filter is returned through a pipe 25 to a pipe 21 joining the circulating-bed furnace 6 and the spray-evaporation step  
30 8.

The further concentrated spent liquor, containing organic matter in addition to ash

and dust, which liquor flows from the spray-evaporation step through the connecting pipe 21, is combusted in the circulating-bed 6 with air 19 at such a high temperature that the heat content of the spent liquor can be recovered, without forming any melt therein, but rather ash accumulated at the bottom of the furnace is discharged through pipe 31 to an ash-dissolving step 7, to which also water 23 is fed. From the dissolv-  
5 ing step, the aqueous solution containing Na aluminate is passed through pipe 24 to a filtering step 10, wherefrom the filtration residue 27 is removed from the process, while the purified solution liquor is fed through a re-circulation pipe 28 to the bleaching step 3 and partially also to the impregnation step 1, if necessary, together  
10 with a supply of fresh Na aluminate 12.

Instead of a circulating-bed furnace 6, any other conventional furnace can be used, e.g., a rotary kiln or a fluidized-bed furnace. Compared to a soda recovery boiler, these devices are substantially less costly and they offer a much easier combustion  
15 control than the soda recovery boiler.

### Example

Wood chips impregnated with sodium sulfite and having an initial brightness of 60.6 prior to bleaching was bleached with hydrogen peroxide in an amount of 1.5 % of the  
20 dry weight of chips when an equal amount of caustic soda in the reference test and an equal amount of sodium aluminate in the comparative test was present. The average of a plurality of tests showed that in a bleaching process, when caustic soda was used for controlling the pH, the pulp brightness increased to 68.6 units, that is by 8 units,  
25 and when sodium aluminate was used the pulp brightness increased up to almost the same level, namely by 6.6 units to 67.2 units. In both test series the bleaching was carried out at the same temperature of 65 °C. However, heat and chemical recovery from spent liquor containing sodium aluminate is substantially easier and more cost-efficient than from spent liquor containing caustic soda.

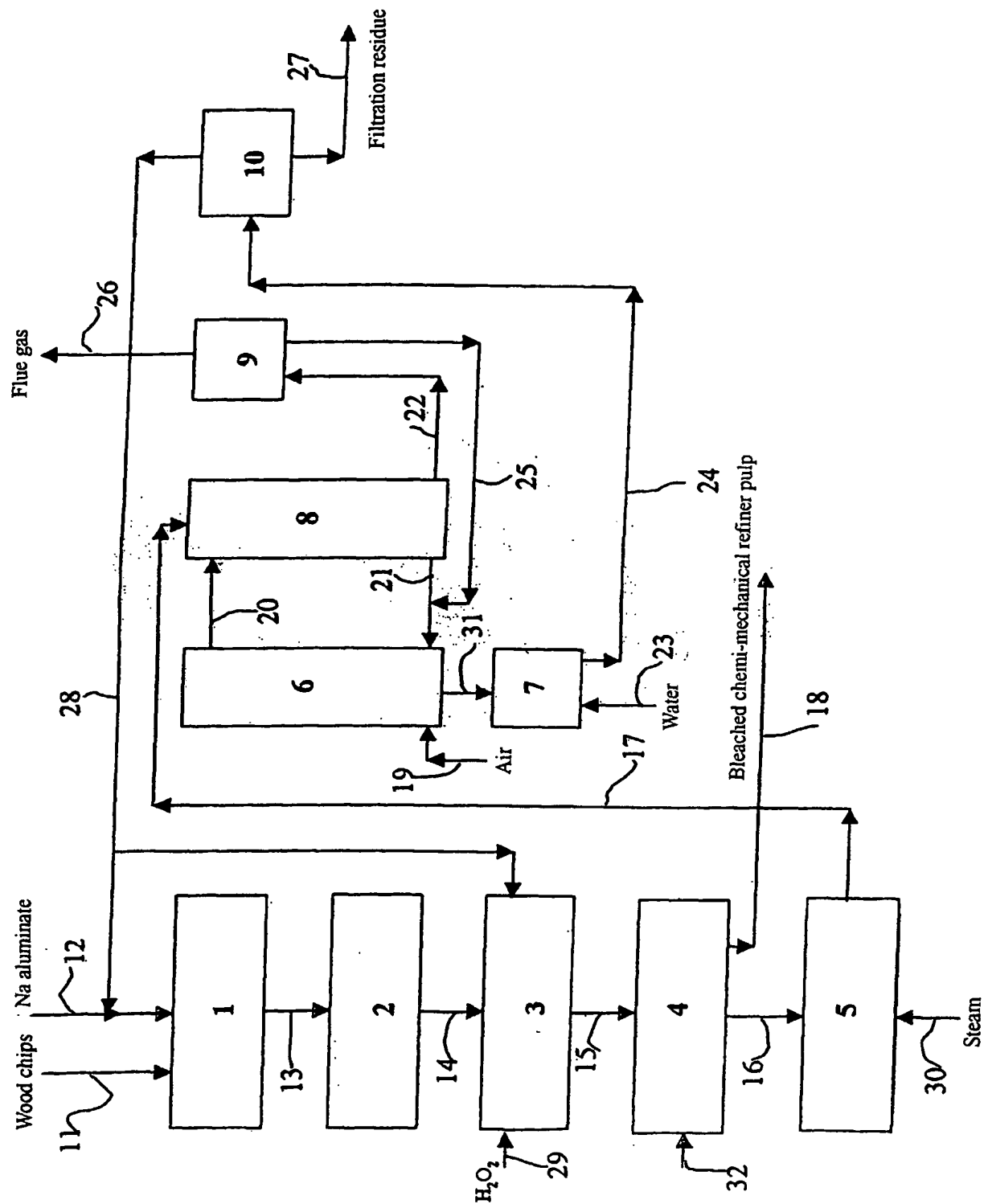
## Claims:

1. A method for bleaching (3) mechanically (2) defibered pulp (14) with peroxide (29) in alkaline conditions and for washing (4) the bleached pulp (15) and recovering chemicals from the spent liquor (16) of the bleaching step by concentrating (5, 8) and  
5 combusting (6) the spent liquor and dissolving (7) the ash (31) thus formed into water (13), **characterized** in that the alkaline conditions in the bleaching step (3) are obtained by adding alkali metal aluminate (12) to the pulp (14) to be bleached, which alkali metal aluminate at least to a part is said ash (28) dissolved in water.
- 10 2. The method of claim 1, **characterized** in that said alkali metal aluminate is sodium aluminate.
- 15 3. The method of claim 2, **characterized** in that said alkaline conditions in the bleaching step (3) are partially obtained by impregnating (1) said wood chips (11) to be mechanically defibered with an aqueous solution (12, 28) of sodium aluminate and passing the pulp (14) after the mechanical defibering step (2) to said bleaching step (3).
- 20 4. The method of claim 3, **characterized** in that the impregnation step (1) of said wood chips (11) to be mechanically defibered at least partially utilizes the ash (28) dissolved in water.
- 25 5. The method of any of the previous claims, **characterized** in that the bleaching step (3) is carried out at a temperature of about 20-150 °C, advantageously 50-100 °C.
- 30 6. The method of any of the previous claims, **characterized** in that the pH of said bleaching step (3) is adjusted to value of about 9.5-12.5, preferably 10-12.
7. The method of any of the previous claims, **characterized** in that the concentrated

(5, 8) spent liquor (21) of said bleaching step (3) is combusted (6) at a temperature of 500-1100 °C.

5 8. The method of any of the previous claims, **characterized** in that the spent liquor (16) received from the bleaching step (3) is concentrated (5) to a solids content of at least about 30 %, preferably 35-45 %.

10 9. The method of claim 8, **characterized** in that the concentrated spent liquor (17) of said bleaching step (3) is further concentrated with hot flue gases (20) discharged from the combusting step (6) of said spent liquor.



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 03/00051

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: D21C 9/16, D21B 1/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: D21C, D21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DATABASE WPI Week 198127 Derwent Publications Ltd., London, GB; Class F09, AN 1981-48892D & JP 56 058086 A (AGENCY OF IND SCI & TECHNOLOGY), 20 May 1981 (1981-05-20) abstract  --	1-9
Y	US 4116759 A (JAN JANSON), 26 Sept 1978 (26.09.78), column 1, line 31 - line 41; column 3, line 35 - line 37; column 4, line 8 - line 10  --	1-9
Y	US 4388148 A (RICHARD A. YAHMARKT ET AL), 14 June 1983 (14.06.83), column 4, line 11 - line 14, claim 1  --	3-4

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"&amp;" document member of the same patent family

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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI/83/00051

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Papper och Trä, Volume 6-7, 1977, Jan Janson, "The use of unconventional alkali in cooking and bleaching" page 425 - page 430 --	1-9
A	DATABASE WPI Week 198345 Derwent Publications Ltd., London, GB; Class E33, AN 1983-813561 & SU 988939 A (CELLULOSE PAPER IND RES), 15 January 1983 (1983-01-14) abstract --	3-4
A	US 2601110 A (JOHN HENRY FISHER ET AL), 17 June 1952 (17.06.52) -- -----	1-9

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

29/03/03

International application No.

PCT/FI 000051

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
US	4116759	A	26/09/78	AU	499100 B	05/04/79
				AU	1712276 A	02/03/78
				BR	7605508 A	16/08/77
				CA	1087355 A	14/10/80
				FI	53141 B,C	31/10/77
				FI	752463 A	03/03/77
				JP	1307302 C	13/03/86
				JP	52042901 A	04/04/77
				JP	60029796 B	12/07/85
				NO	150807 B,C	10/09/84
				NO	762969 A	03/03/77
				NZ	181792 A	11/01/79
				SE	7609675 A	03/03/77
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US	4388148	A	14/06/83	NONE		
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US	2601110	A	17/06/52	NONE		